THERMODYNAMIC PROPERTIES OF METHYLENE CHLORIDE

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ABSTRACT

Thermodynamic properties of methylene chloride have been computed upto a temperature of 750° *K* and a pressure of 200 atmospheres using Martin and Hou Equation of State. The results are presented in tabular form and as an entropy-temperature diagram.

INTRODUCTION

Methylene chloride is used as a refrigerant and hence a knowledge of its thermodynamic properties is necessary. A detailed literature survey revealed that the thermodynamic properties of methylene chloride are available only upto a temperature of $423^\circ K$ and a pressure of about 2.6 atmospheres.

In the present work, tables and a diagram of thermodynamic properties of methylene chloride upto a temperature of $750^\circ K$ and a pressure of 200 atmospheres are presented.

SURVEY OF EXISTING DATA

1. *Critical Constants* : The critical pressure and temperature of methylene chloride as given by Kobe and Lynn[6] have been used for the present investigation.

The critical volume of methylene chloride was calculated using Meissner's[10] method, Vowel's[10] method, and by extrapolating the rectilinear diameter to the critical temperature. The critical volume calculated by the last method was found to be in good agreement with the critical volumes calculated by Meissner's and Vowel's method, and hence was accepted for the present investigation.

Thus, the critical constants used in this work are :

$$T_c = 510.0^\circ K$$

$$P_c = 60.0 \text{ atmospheres}$$

$$V_c = 0.181 \text{ litres/mole.}$$

2. *Vapour Pressure*: The vapour pressure of methylene chloride has been determined by Dzung[1], Perry[8] and Rex[9]. The vapour pressure data of these investigators [1, 8, 9] were smoothed. The smoothened data along with the accepted critical point were fitted using the least square technique to the equation

$$\log P = a + b/T + c \log T + dT \quad [1]$$

where,

$$a = -43.339853$$
$$b = -138.496091$$
$$c = 19.09293135$$
$$d = -1.23646264 \times 10^{-2}$$

The maximum and average absolute deviations were found to be 0.9% and 0.25% respectively. The vapour pressures beyond the range of available data were calculated using Equation [1].

3. *Specific volumes of Saturated liquid and Vapour*: The densities of saturated liquid and vapour have been determined by Dzung[1] upto a temperature of 343°K. Saturated liquid densities over the range of temperature of 273 – 303°K have been determined by Griffing *et al.*[4].

The saturated vapour densities of methylene chloride. at temperatures above 343°K were calculated up to the critical point using the Martin and Hou Equation of State (Equation 4) at the corresponding vapour pressures.

The saturated liquid densities of Dzung and Griffing *et al.* were smoothened. The smoothened saturated liquid densities, the vapour densities of Dzung, and the calculated vapour densities were plotted and a smooth curve was drawn. The saturated liquid and vapour densities accepted for the present work were taken from the smooth curve taking into consideration the observance of the law of rectilinear diameter.

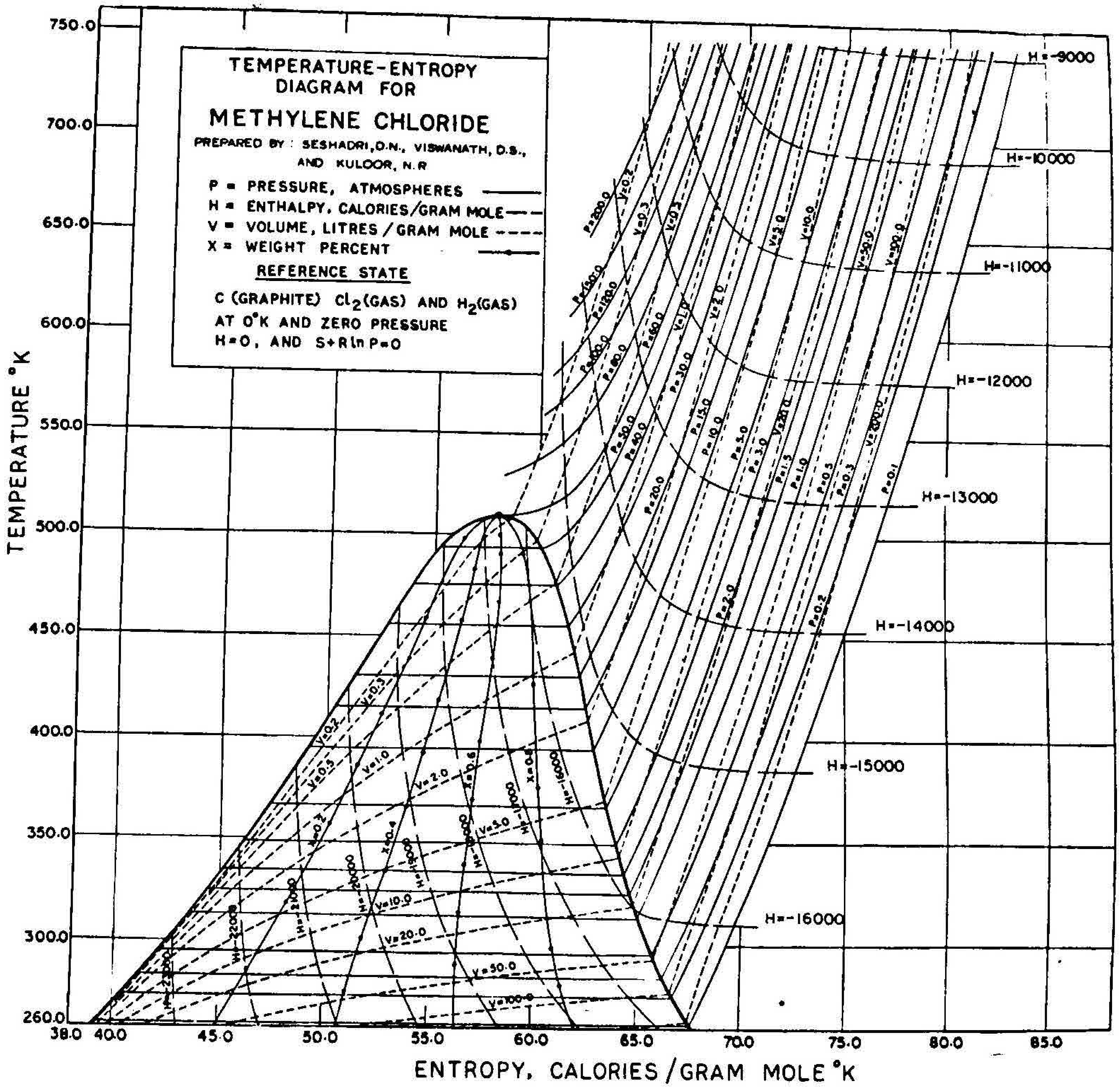
4. *Heat Capacity of the Ideal Gas*: The heat capacity of methylene chloride in the ideal gaseous state has been determined using spectroscopic data upto a temperature of 1500°K by Gelles and Pitzer[2] and upto 600°K by Glockler and Edgell[3]. The spectroscopic data used by Gelles and Pitzer are more recent and their data cover a wider range. Hence the data of Gelles and Pitzer have been utilized for the present investigation.

The smoothened data of Gelles and Pitzer were fitted over a range of temperature of 273 – 1500°K to the equation,

$$C_p^* = A + BT + CT^2 + DT^3 \quad [2]$$

where,

$$A = 7.1083$$
$$B = 3.6969 \times 10^{-2}$$
$$C = -2.9613 \times 10^{-5}$$
$$D = 8.4214 \times 10^{-9}.$$


TEMPERATURE-ENTROPY DIAGRAM FOR
METHYLENE CHLORIDE
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P = PRESSURE, ATMOSPHERES
H = ENTHALPY, CALORIES/GRAM MOLE
V = VOLUME, LITRES / GRAM MOLE
X = WEIGHT PERCENT
REFERENCE STATE
C (GRAPHITE) Cl2(GAS) AND H2(GAS)
AT 0°K AND ZERO PRESSURE
H=0, AND S+R ln P=0
TEMPERATURE °K
ENTROPY, CALORIES / GRAM MOLE °K
750.0
700.0
650.0
600.0
550.0
500.0
450.0
400.0
350.0
300.0
260.0
38.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
75.0
80.0
85.0
H=-9000
H=-10000
H=-11000
H=-12000
H=-13000
H=-14000
H=-15000
H=-16000
H=-16000
H=-17000
H=-18000
H=-19000
H=-20000
H=-21000
H=-22000
H=-23000
P=200.0
P=150.0
P=120.0
P=100.0
P=80.0
P=60.0
P=50.0
P=40.0
P=30.0
P=20.0
P=15.0
P=10.0
P=5.0
P=3.0
P=2.0
P=1.5
P=1.0
P=0.5
P=0.3
P=0.2
P=0.1
V=0.2
V=0.3
V=0.5
V=1.0
V=2.0
V=5.0
V=10.0
V=20.0
V=50.0
V=100.0
V=200.0
X=0.2
X=0.4
X=0.6
X=0.8

Fig. 1

The maximum and average absolute deviations were found to be 0.46% and 0.15% respectively. Equation [2] has been used for the present investigation.

5. *Heat Capacity of the Saturated Liquid*: The heat capacity of saturated liquid has been presented by Dzung[1]. These data have been utilized in checking the internal consistency of the tabulated results.

6. *Latent Heat of Vaporization*: The heats of vaporization of methylene chloride have been presented by Dzung[3]. These data were fitted to an equation of the form:

$$\lambda = \lambda_0 (T_c - T)^n \qquad [3]$$

with $n = 0.41$ and $\lambda_0 = 9.062$.

The maximum and average absolute deviations of calculated values of heats of vaporization, in the range of available data were found to be 0.1% and 0.04% respectively. For this work, Equation [3] has been accepted for the calculation of latent heats of vaporization.

CALCULATION OF THERMODYNAMIC PROPERTIES

For the calculation of thermodynamic properties, Martin and Hou Equation of State,

$$P = \frac{RT}{(V - B_0)} + \frac{A_2 + B_2 T + C_2 e^{-KT/T_c}}{(V - B_0)^2} + \frac{A_3 + B_3 T + C_3 e^{-KT/T_c}}{(V - B_0)^3} + \frac{A_4}{(V - B_0)^4} + \frac{B_5 T + C_5 e^{-KT/T_c}}{(V - B_0)^5} \qquad [4]$$

with $K = 5.475$ has been used.

The constants in Equation [4] evaluated following the procedures outlined the authors[7] are:

$B_0 = 3.307556 \times 10^{-2}$
$A_2 = -16.355163$
$B_2 = 1{\cdot}1851555 \times 10^{-2}$
$C_2 = -333.17645$
$A_3 = 2.1346826$
$B_3 = -1.412630 \times 10^{-3}$
$C_3 = 54.635205$
$A_4 = -0.11580094$
$B_5 = 7.3944412 \times 10^{-6}$
$C_5 = -0.11707260$

In the range of available data, Equation [4] was found to predict pressures satisfactorily. Comparison could not be made above a pressure of 2.6 atmospheres because of lack of data.

Specific volumes of saturated and superheated vapour were calculated using Equation [4] by making use of Newton-Raphson iterative method on IBM 1620 digital computer, for various temperatures and pressures.

Entropy and Enthalpy of Superheated Vapour: Considering the entropy and enthalpy to be functions of volume and temperature, we have:

$$dS = \left(\frac{\partial P}{\partial T}\right)_V dV + \frac{C_V}{T} dT \qquad [5]$$

Making use of the relation, $dH = TdS + VdP$, we get:

$$dH = [C_P\, dT_P + d(PV)_T - P dV_T + T(\partial P/\partial T)_V dV_T] \qquad [6]$$

Using Equations [4] and [2] and taking the necessary derivatives and substituting in Equations [5] and [6] we get the expressions for entropy and enthalpy as follows:

$$\begin{aligned} S = {} & R \ln (V - B_0) - \{B_2/(V - B_0)\} - \{B_3/2\,(V - B_0)^2\} - \{B_5/4\,(V - B_0)^4\} \\ & + [C_2/(V - B_0) + C_3/2\,(V - B_0)^2 + C_5/4\,(V - B_0)^4](K/T_c)\, e^{-KT/T_c} \\ & + (A - R) \ln T + BT + (C/2)\, T^2 + (D/3)\, T^3 + C_S \end{aligned} \qquad [7]$$

and

$$\begin{aligned} H = {} & (A - R)\, T + (B/2)\, T^2 + (C/3)\, T^3 + (D/4)\, T^4 \\ & + \frac{A_2 + (1 + KT/T_c)\, C_2\, e^{-KT/T_c}}{(V - B_0)} \\ & + \frac{A_3 + (1 + KT/T_c)\, C_2 e^{-KT/T_c}}{2\,(V - B_0)^2} + \frac{A_4}{3\,(V - B_0)^3} \\ & + \frac{A_5 + (1 + KT/T_c)\, C_5\, e^{-KT/T_c}}{4\,(V - B_0)^4} + PV + C_H \end{aligned} \qquad [8]$$

where, C_S and C_H are the constants of integration.

$S + R \ln P = 0$ and $H = 0$ for elements at 0°K and zero pressure was taken to be the reference point. The entropy and enthalpy of the saturated vapour at the boiling point were calculated using the ideal gas thermodynamic properties, the heats of formation and Berthelot's correction for entropy and enthalpy. Using the values of entropy and enthalpy at the boiling point, the constants of integration, C_S and C_H were evaluated.

The values of entropy and enthalpy were calculated at various temperatures and pressures using Equations [7] and [8].

ENTROPY AND ENTHALPY OF SATURATED VAPOUR

As Martin and Hou Equation of State (Equation 4) holds good for the saturated vapour region also, the properties of saturated vapour were calculated in the same manner as in the superheated vapour region.

ENTROPY AND ENTHALPY OF SATURATED LIQUID

The latent heat of vaporization of methylene chloride was calculated using Equation [3].

The entropy of vaporization ΔS_V, is related to the heat of vaporization, by the relation,

$$\Delta H_V = T \Delta S_V \qquad [9]$$

The entropies and enthalpies of saturated liquid were calculated using the equations,

$$S_l = S_g - \Delta S_V \qquad [10]$$

and

$$H_l = H_g - \Delta H_V \qquad [11]$$

The properties of saturated and superheated methylene chloride are presented in Tables I and II respectively, and in graphical form as Figure I.

INTERNAL CONSISTENCY OF THE TABULATED RESULTS

The internal consistency of the results was checked by two methods as outlined below.

(*a*) *Using $dH = TdS + VdP$*: The relation, $dH = TdS + VdP$ may be used to check the internal consistency of the entropy and enthalpy values.

At constant pressure,

$$dH = TdS \qquad [12]$$

Hence $dH = d(TS) - SdT$, from which

$$H\Big]_1^2 = T_2S_2 - T_1S_1 - \int_1^2 SdT \qquad [13]$$

TABLE I

Properties of Saturated Liquid and Vapour

T°K	P Atms.	V_l	V_g	S_l	ΔS_v	S_g	H_l	ΔH_v	H_g
260.0	0.0919	0.0611	230.5	39.26	28.47	67.73	−24011	7402	−16609
270.0	0.1566	0.0620	140.1	40.13	26.96	67.09	−23780	7280	−16500
280.0	0.2555	0.0629	88.66	40.97	25.55	66.52	−23547	7154	−16393
290.0	0.4003	0.0637	58.30	41.80	24.22	66.02	−23311	7025	−16286
300.0	0.6073	0.0646	39.48	42.58	22.98	65.56	−23074	6893	−16181
310.0	0.8842	0.0656	27.80	43.39	21.79	65.18	−22832	6755	−16077
320.0	1.2740	0.0666	19.73	44.13	20.67	64.80	−22593	6615	−15978
330.0	1.7610	0.0676	14.56	44.88	19.61	64.49	−22350	6471	−15879
340.0	2.3990	0.0686	10.87	45.60	18.59	64.19	−22104	6320	−15784
350.0	3.2400	0.0699	8.151	46.29	17.61	63.90	−21861	6165	−15696
360.0	4.2800	0.0711	6.233	46.95	16.68	63.63	−21616	6004	−15612
370.0	5.564	0.0725	4.826	47.60	15.78	63.38	−21371	5837	−15534
380.0	7.124	0.0741	3.780	48.24	14.90	63.14	−21125	5662	−15463
390.0	8.990	0.0757	2.992	48.86	14.05	62.91	−20879	5480	−15399
400.0	11.20	0.0775	2.389	49.43	13.22	62.65	−20632	5288	−15344
410.0	13.76	0.0794	1.924	50.07	12.40	62.47	−20383	5085	−15298
420.0	16.70	0.0817	1.559	50.67	11.59	62.26	−20131	4869	−15262
430.0	20.04	0.0841	1.271	51.26	10.79	62.05	−19880	4641	−15239
440.0	23.78	0.0867	1.041	51.86	9.98	61.84	−19621	4393	−15228
450.0	27.92	0.0899	0.8548	52.45	9.16	61.61	−19358	4124	−15234
460.0	32.45	0.0936	0.7012	53.04	8.32	61.36	−19089	3827	−15262
470.0	37.35	0.0985	0.5730	53.65	7.43	61.08	−18807	3492	−15315
475.0	39.92	0.1016	0.5166	53.97	6.96	60.93	−18662	3306	−15356
480.0	42.59	0.1050	0.4632	54.28	6.47	60.75	−18515	3104	−15411
485.0	45.33	0.1092	0.4143	54.60	5.94	60.54	−18355	2879	−15476
490.0	48.15	0.1148	0.3693	54.97	5.36	60.33	−18183	2628	−15555
495.0	51.03	0.1213	0.3217	55.31	4.72	60.03	−18014	2336	−15678
500.0	53.96	0.1297	0.2785	55.72	3.96	59.68	−17798	1978	−15820
505.0	56.95	0.1420	0.2340	56.38	2.95	59.33	−17510	1489	−16021
510.0	60.00	0.1810	0.1810	58.58	0.00	58.58	−16600	0	−16600

TABLE II
Properties of Superheated Vapour

(Pressure range 0.1 to 5.0 atms.)

T°K↓	P Atms.→	0.1	0.2	0.3	0.5	1.0	2.0	3.0	5.0
280.0	V	228.5	113.6						
	H	– 16374	– 16386						
	S	68.43	67.03						
300.0	V	245.1	122.1	81.02	48.19				
	H	– 16131	– 16141	– 16150	– 16170				
	S	69.27	67.87	67.04	65.98				
320.0	V	261.7	130.4	86.67	51.65	25.38			
	H	– 15880	– 15888	– 15896	– 15912	– 15954			
	S	70.08	68.68	67.86	66.81	65.33			
340.0	V	278.3	138.8	92.27	55.07	27.16	13.19		
	H	– 15621	– 15628	– 15634	– 15648	– 15683	– 15754		
	S	70.87	69.47	68.65	67.61	66.16	64.62		
360.0	V	294.8	147.1	97.85	58.46	28.92	14.13	9.197	
	H	– 15354	– 15360	– 15366	– 15377	– 15406	– 15466	– 15528	
	S	71.63	70.24	69.42	68.38	66.95	65.45	64.51	
380.0	V	311.3	155.4	103.4	61.83	30.65	15.05	9.841	5.664
	H	– 15080	– 15085	– 15090	– 15100	– 15124	– 15174	– 15226	– 15335
	S	72.37	70.98	70.17	69.13	67.71	66.24	65.33	64.10
400.0	V	327.8	163.7	108.9	65. 8	32.36	15.94	10.46	6.075
	H	– 14799	– 14803	– 14807	– 14815	– 14836	– 14879	– 14922	– 15014
	S	73.09	71.71	70.89	69.85	68.45	66.99	66.11	64.92
420.0	V	344.2	171.9	114.5	68.52	34.06	16.82	11.07	6.468
	H	– 14510	– 14514	– 14518	– 14525	– 14543	– 14579	– 14616	– 14694
	S	73.79	72.41	71.60	70.57	69.16	67.72	66.86	65.70
440.0	V	360.7	180.2	120.0	71.85	35.74	17.69	11.67	6.849
	H	– 14215	– 14218	– 14221	– 14228	– 14243	– 14275	– 14307	– 14374
	S	74.48	73.10	72.29	71.26	69.86	68.43	67.57	66.45

TABLE II—(*contd.*)

Properties of Superheated Vapour

(Pressure range 0.1 to 5.0 atms.)

T°K ↓	P.Atms.→	0.1	0.2	0.3	0.5	1.0	2.0	3.0	5.0
460.0	V	377.1	188.4	125.5	75.17	37.43	18.55	12.26	7.220
	H	−13913	−13916	−13918	−13924	−13938	−13966	−13994	−14052
	S	75.15	73.77	72.96	71.94	70.54	69.12	68.27	67.16
480.0	V	393.6	196.6	131.0	78.49	39.10	19.40	12.84	7.583
	H	−13604	−13607	−13609	−13614	−13627	−13651	−13676	−13727
	S	75.81	74.43	73.62	72.60	71.20	69.79	68.95	67.86
500.0	V	410.0	204.9	136.5	81.80	40.77	20.25	13.41	7.941
	H	−13290	−13292	−13294	−13298	−13309	−13332	−13354	−13399
	S	76.45	75.07	74.26	73.24	71.85	70.44	69.60	68.53
520.0	V	426.5	213.1	142.0	85.10	42.43	21.10	13.99	8.295
	H	−12969	−12971	−12973	−12977	−12987	−13006	−13027	−13067
	S	77.08	75.70	74.89	73.87	72.48	71.08	70.25	69.18
540.0	V	442.9	221.3	147.5	88.41	44.09	21.94	14.55	8.645
	H	−12642	−12644	−12646	−12649	−12658	−12676	−12695	−12731
	S	77.70	76.32	75.51	74.49	73.10	71.70	70.87	69.81
560.0	V	459.3	229.6	153.0	91.71	45.75	22.78	15.12	8.992
	H	−12310	−12312	−12313	−12316	−12325	−12341	−12358	−12391
	S	78.30	76.92	76.11	75.09	73.71	72.31	71.48	70.43
580.0	V	475.8	237.8	158.5	95.01	47.41	23.62	15.68	9.337
	H	−11972	−11974	−11975	−11978	−11986	−12001	−12016	−12047
	S	78.89	77.51	76.71	75.69	74.30	72.91	72.08	71.03
600.0	V	492.2	246.0	163.9	98.30	49.07	24.45	16.25	9.680
	H	−11629	−11630	−11632	−11634	−11642	−11656	−11670	−11698
	S	79.47	78.10	77.29	76.27	74.89	73.49	72.67	71.62
620.0	V	508.6	254.2	169.4	101.6	50.72	25.28	16.81	10.02
	H	−11281	−11282	−11283	−11286	−11292	−11306	−11319	−11345
	S	80.05	78.67	77.86	76.84	75.46	74.07	73.25	72.20

TABLE II

Properties of Superheated Vapour

(Pressure range 0.1 to 5.0 atms.)

T°K ↓	P. Atms.→	0.1	0.2	0.3	0.5	1 0	2.0	3.0	5.0
640.0	V	525.0	262.4	174 9	104.9	52.38	26.12	17.36	10.36
	H	– 10928	– 10929	– 10930	– 10932	– 10939	– 10951	– 10963	– 10988
	S	80.61	79.23	78 42	77.40	76.02	74 63	73.81	72.77
660.0	V	541.4	270.7	180.3	108.2	54 03	26.95	17.92	10.70
	H	– 10570	– 10571	– 10572	– 10574	– 10580	– 10592	– 10603	– 10626
	S	81.16	79.78	78.97	77.95	76.57	75.18	74 37	73.33
680.0	V	557.9	278.9	185.9	111.5	55.68	27.78	18.48	11.04
	H	– 10207	– 10208	– 10210	– 10212	– 10217	– 10228	– 10239	– 10261
	S	81.70	80.32	79.51	78 50	77.11	75.72	74 91	73.87
700.0	V	574.3	287.1	191.4	114.8	57.33	28.61	19.04	11.38
	H	– 9841	– 9842	– 9843	– 9845	– 9850	– 9860	– 9870	– 9891
	S	82.23	80.85	80.04	79.03	77.65	76.26	75.44	74.41
720.0	V	590.7	295.3	196.8	118.1	58.98	29.44	19.59	11.71
	H	– 9470	– 9471	– 9472	– 9474	– 9478	– 9488	– 9498	– 9517
	S	82.75	81.37	80.57	79.55	78.17	76.78	75.97	74.93
750.0	V	615.3	307.6	205.1	123.0	61.45	30.68	20.42	12.22
	H	– 8906	– 8906	– 8907	– 8909	– 8914	– 8923	– 8932	– 8950
	S	83.52	82.14	81.33	80.32	78.94	77.55	76.74	75.71

TABLE II—(*contd.*)

Properties of Superheated Vapour

(Pressure range 10.0 to 200.0 atms.)

T°K ↓	P. Atms.→	10.0	20.0	30.0	50.0	100.0	150.0	200.0
400.0	V	2.751						
	H	– 15273						
	S	63.05						
420.0	V	2.996						
	H	– 14907						
	S	63.95						
440.0	V	3.221	1.362					
	H	– 14553	– 15000					
	S	64.77	62.61					
460.0	V	3.433	1.512	0.8231				
	H	– 14206	– 14567	– 15077				
	S	65.54	63.57	61.86				
480.0	V	3.636	1.644	0.9556				
	H	– 13861	– 14164	– 14545				
	S	66.27	64.42	63.00				
500.0	V	3.832	1.766	1.062	0.4266			
	H	– 13517	– 13776	– 14085	– 15101			
	S	66.98	65.21	63.94	61.22			
520.0	V	4.023	1.879	1.155	0.5461			
	H	– 13172	– 13400	– 13659	– 14347			
	S	67.65	65.95	64.77	62.71			
540.0	V	4.210	1.987	1.240	0.6265			
	H	– 12826	– 13028	– 13252	– 13795			
	S	68.31	66.66	65.54	63.74			
560.0	V	4.394	2.092	1.320	0.6931	0.1692		
	H	– 12477	– 12659	– 12855	– 13309	– 15336		
	S	68.94	67.33	66.26	64.63	60.18		

Table II — (*concld.*)

Properties of Superheated Vapour

(Pressure range 10.0 to 200 atms.)

T°K	P. Atms.	10.0	20.0	30.0	50.0	100.0	150.0	200 0
580.0	V	4.576	2.193	1.396	0.7520	0.2473		
	H	– 12126	– 12290	– 12466	– 12858	– 14240		
	S	69.56	67.97	66.95	65.42	62.10		
600.0	V	4.755	2.291	1.468	0.8061	0.2991		
	H	– 11771	– 11921	– 12080	– 12425	– 13518		
	S	70.16	68.60	67.60	66.15	63.33		
620.0	V	4.933	2.388	1.538	0.8561	0.3407	0.1672	
	H	– 11412	– 11551	– 11695	– 12005	– 12922	– 14059	
	S	70.75	69.21	68.23	66.84	64.31	62.00	
640.0	V	5.110	2.483	1.607	0.9048	0.3767	0.2015	
	H	– 11050	– 11179	– 11312	– 11592	– 12388	– 13309	
	S	71.32	69.80	68.84	67.49	65.15	63.19	
660.0	V	5.286	2.577	1.674	0.9510	0.4092	0.2309	0.1488
	H	– 10685	– 10804	– 10928	– 11185	– 11890	– 12668	– 13418
	S	71.88	70.37	69.43	68.12	65.92	64.18	62.70
680.0	V	5.460	2.670	1.740	0.9957	0.4392	0.2566	0.1677
	H	– 10316	– 10428	– 10542	– 10779	– 11515	– 12093	– 12786
	S	72.44	70.94	70.01	68.73	66.63	65.04	63.65
700.0	V	5.634	2.762	1.804	1.039	0.4674	0.2799	0.1878
	H	– 9943	– 10047	– 10155	– 10375	– 10955	– 11558	– 12172
	S	72.98	71.49	70.57	69.31	67.30	65.81	64.54
720.0	V	5.807	2.853	1.868	1.082	0.4941	0.3015	0.2068
	H	– 9566	– 9666	– 9766	– 9972	– 10505	– 11049	– 11596
	S	73.51	72.03	71.11	69.88	67.93	66.53	65.35
750.0	V	6.065	2.988	1.963	1.144	0.5322	0.3316	0.2328
	H	– 8995	– 9086	– 9179	– 9366	– 9842	– 10319	– 10789
	S	74.28	72.81	71.91	70.71	68.83	67.52	66.45

The definite integral in Equation (13) was evaluated by using Simpson's rule. Table III gives the deviations of the changes of enthalpy ΔH, for six isobars. It can be seen from Table III that the calculated values agree very well with those calculated using the tabulated enthalpies. Hence the tabulated data are internally consistent.

(*b*) *Using the heat capacity of saturated liquid*: It is possible to show[5] that the heat capacity of saturated liquid (C_S^l) and the heat capacity of gas at constant volume are related by the Equation,

$$C_S^1 = C_V - V_1 (dP/dT)_S - \frac{d(\Delta H_V)}{dT} + V_g(dP/dT)_{V_g}$$

$$+ [T(dP/dT)_{V_g} + V_g (dP/dV_g)_T] (dV_g/dT)_S \qquad [14]$$

Also,

$$C_V = C_V^* + \int_\infty^V T(d^2P/dT^2)_V \, dV \qquad [15]$$

Using the Equations 1, 2, 3 and 4 in Equations [14] and [15], it is possible to calculate the heat capacity of saturated liquid.

Table IV gives the deviations of calculated and available saturated liquid heat capacities. The maximum and average deviations were found to be 3.1% and 1.00% respectively. Since the calculation of heat capacities of saturated liquid using the equations [14] and [15] involves first and second derivatives, this serves as a very good check of the equations used, and the internal consistency of the data.

TABLE III

Isobar Atms.	Range of temp. °K	$\Delta H_{calc.}$	ΔH_{tables}	% deviation
0.1	270 – 750	7588.0	7587.4	0.008
1.0	330 – 750	6907.3	6905.3	0.030
10.0	410 – 750	6090.5	6093.1	0.043
50.0	510 – 750	5313.6	5310.4	0.060
100.0	570 – 750	4858.3	4852.1	0.078
200.0	650 – 750	2935.1	2930.7	0.150

TABLE IV

Temp. °*K*	C_S^1(literature)	C_S^1(calculated)	%deviation
250.0	23.341	22.617	3.10
260.0	23.351	22.941	1.76
270.0	23.476	23.227	1.06
280.0	23.522	23.450	0.31
290.0	23.684	23.667	0.07
300.0	23.898	23.856	0.18
310.0	24.162	24.051	0.46

NOMENCLATURE

$A, B, C, D,$	Constants in Equation (2)
$a, b, c, d,$	Constants in Equation (1)
$B_0. A_2, B_2, C_2$ $A_3, B_3, C_3,$ $A_4, B_5\ C_5$	Constant in Equation (4)
C_P	Heat capacity at constant pressure, calories/gram mole °*K*
C_V	Heat capacity at constant volume, calories/gram mole °*K*
H	Enthalpy, calories/gram mole
n	Constant in Equation (3)
P	Pressure, atmospheres
S	Entropy, calories/gram mole °*K*
T	Temperature, °*K*
V	Volume, litres/gram mole
ΔH_V	Enthalpy of vaporization, calories/gram mole
ΔS_V	Entropy of vaporization, calories/gram mole °*K*
λ	Heat of vaporization, calories/gram mole
λ_0	Constant in Equation (3)

SUPERSCRIPT

*	Denotes properties at zero pressure or ideal gaseous state

SUBSCRIPTS

c	Critical point
g	Gas or vapour
P	Pressure
l	Liquid
S	Saturation
T	Temperature
V	Volume

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